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14. ABSTRACT <p>Low concentration polymer networks are used to stabilize various pattern-forming states of cholesteric liquid crystals. The resulting optical diffraction gratings operate with >70% efficiency in transmission (Raman-Nath mode) and are electrically switchable between diffracting and non-diffracting states for low applied voltages (3 - 30 V). A remarkable templating of spatio-orientational order, intrinsic to the liquid crystal pattern formation, is expressed in the polymer network. Based on preliminary results on a dopable polyacetylene, the liquid crystal-based templating effect holds promise as a low cost, simple processing approach to the assembly of micron and submicron, orientationally-ordered arrays of functional polymers.</p>					
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Introduction

This report summarizes the results of our research into the formation of spatially and orientationally anisotropic polymer networks using electric field-induced pattern-forming states of cholesteric liquid crystals as templates. The overall objective was twofold: to use the polymer network to stabilize light-diffracting states of the liquid crystal (thus producing an efficient, low-cost, highly processible and electrically-responsive “on-off” diffraction grating) and second to develop a more general method of templating the high degree of spatio-orientational order that naturally occurs in liquid crystals into functional polymer networks (e.g., conducting polymers). Using a mesogenic diacrylate, we observed a highly efficient one and two-dimensional templating effect, and demonstrated its use in producing voltage and frequency based electrically-switchable polymer-stabilized cholesteric diffraction gratings (PSCDGs). We also showed that planar light diffracting states could be stabilized by micron-thin polymer layers templated at the surfaces of the liquid crystal cell. (In this case, the desirable electro-optic properties of the pure liquid crystal are not affected by the polymer network, as they are to some degree when the network is formed in the bulk.) We also adapted our templating technique to form spatially patterned arrays of conducting polymers – specifically, of a dopable polyacetylene derivative. Finally we have shown that a key feature of the mechanism behind the templating effect is a spatially-periodic phase separation of small droplets of the monomer, prior to polymerization, that is driven by gradients in the elastic and/or electrostatic energy of the liquid crystal host. This spontaneous “internal” phase separation mechanism, together with the high degree of orientational order that is embedded in the polymer network as a result of its use, makes our approach distinct from the more common patterning technique based on optical holography. There is also a clear advantage when polymerization must be initiated by means other than light – e.g., a chemical catalyst as is the case for most conducting polymers.

Materials and Methods

Figure 1 summarizes the major materials used in our studies. The liquid crystals were commercial mixtures with very broad nematic temperature ranges, and were doped with well-known commercial chiral twisting agents to form cholesterics. Except for the work described in the final

section below, the two monomers used were commercial photopolymerizable diacrylates, one of which (RM257) is liquid crystalline. The typical monomer concentration in the initial mixture was 5 wt%, and the concentration of chiral dopant was ~ 0.4 wt%, adjusted to give a cholesteric pitch comparable to the sample thickness. The procedure for forming and polymer-stabilizing the liquid crystal light diffracting states is illustrated in Figure 2.

- LCs: ~94.6 %
BL006: S -20°C N 113°C I, $\Delta n = 0.286$; $\Delta \varepsilon = +17.3$
- Reactive Monomer: ~5%
RM257: S 70°C N 126°C I

$$\text{CH}_2=\text{CHCO}_2(\text{CH}_2)_3\text{O}-\text{C}_6\text{H}_4-\text{CO}_2-\text{C}_6\text{H}_4(\text{CH}_3)-\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{O}-\text{C}(\text{CH}_2)_3\text{O}_2\text{CCH}=\text{CH}_2$$
 HDDA: isotropic monomer

$$\text{CH}_2=\text{CHCO}_2(\text{CH}_2)_6\text{O}_2\text{CCH}=\text{CH}_2$$
- Chiral dopants: ~0.4 %
R1011:

$$\text{H}_{11}\text{C}_3-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CO}_2-\text{C}(\text{H})(\text{C}_6\text{H}_5)-\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}_3\text{H}_{11}$$
- Photoinitiator: 5 % of monomer
Irgacure 651:

$$\text{C}_6\text{H}_5-\text{C}(\text{O})=\text{C}(\text{OCH}_3)-\text{C}_6\text{H}_5$$

Figure 1: Liquid crystal and monomer materials.

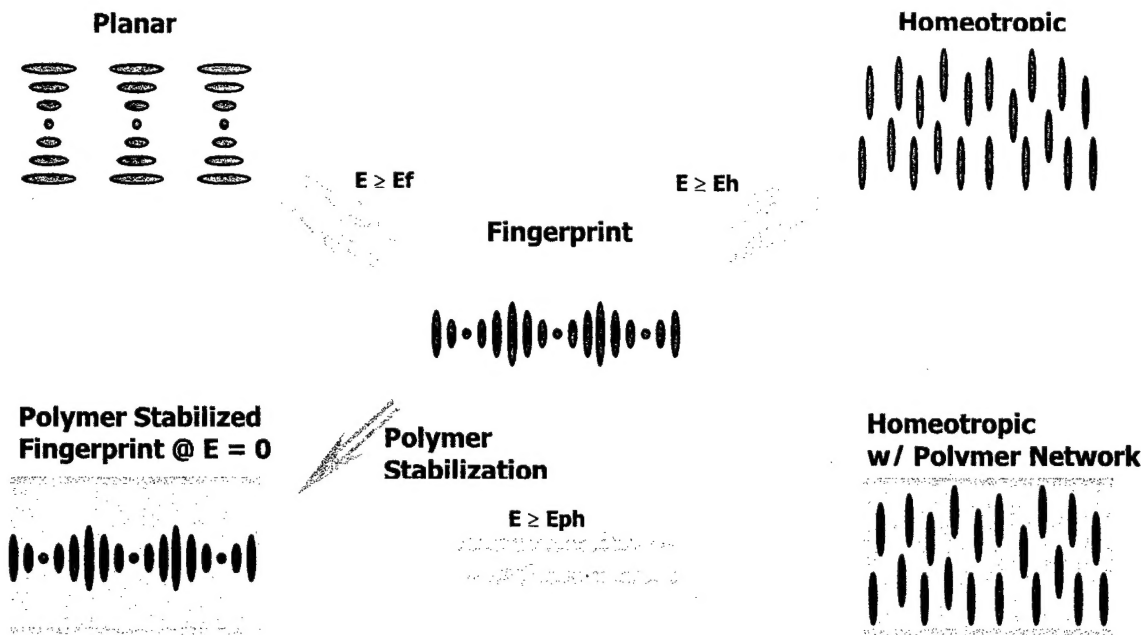


Figure 2: Schematic of procedure for producing PSCDGs and various electrically-switchable optical states.

The sample was contained in a commercially available electro-optic cell with a 10-micron gap between the inner surfaces. These surfaces were coated with a conducting (indium tin oxide) layer and overcoated with a rubbed polyimide alignment layer. An AC electric field was applied across the cell, inducing a reorientation and distortion of the helical axis of the cholesteric, which was initially perpendicular to the substrates. In this way, planar diffracting states are produced. Figure 3 shows a phase diagram, indicating the variety of pattern-forming, light diffracting states accessible with varying sample thickness to pitch ratio

and frequency of applied field (above the threshold of a few tenths of volt per micron required to induce the pattern formation).

The planar light-diffracting states were locked in by photopolymerization of the low concentration monomer component using UV light of two wavelengths: 365 nm (which transmitted through the sample at

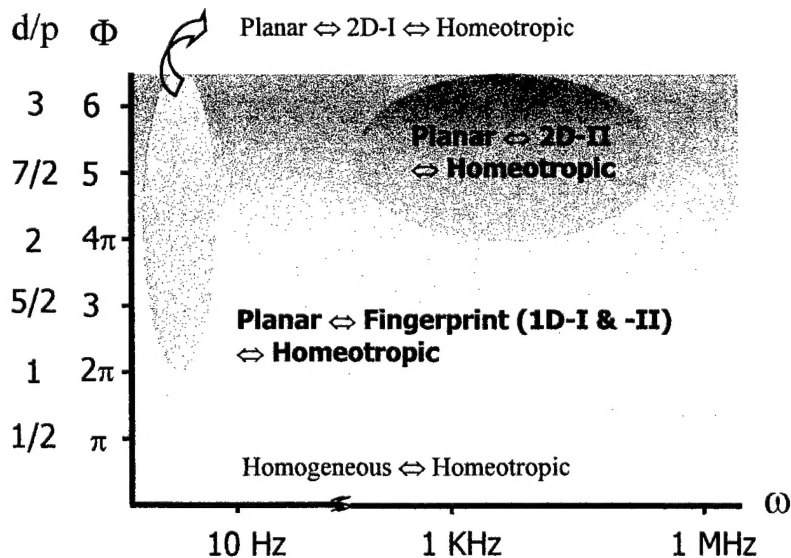


Figure 3: Phase diagram for pattern-forming states of a cholesteric liquid crystal subject to homogeneous anchoring conditions and an applied electric field along the helical axis.

nearly 100%) to form bulk stabilizing networks and 322 nm (which was strongly absorbed) to form thin-layer surface networks that were also found to efficiently stabilize the light diffracting states. The UV intensity was typically between 0.01 and 0.1 mW/cm², and the typical exposure time was 30 min.

Electrically responsive diffraction gratings

Once anchored by the polymer network, the planar diffraction states were stable against removal of the field applied to induce them in the first place. Thus in zero-field, the grating is in the "ON" state. However, upon application of a larger field (typically a few V/ μ m), the liquid crystal molecules (anchored by van der Waals forces but not chemically bound to the network) could be made to rotate so that their optic axis was vertical to the substrates ("hometropic" state). In this state,

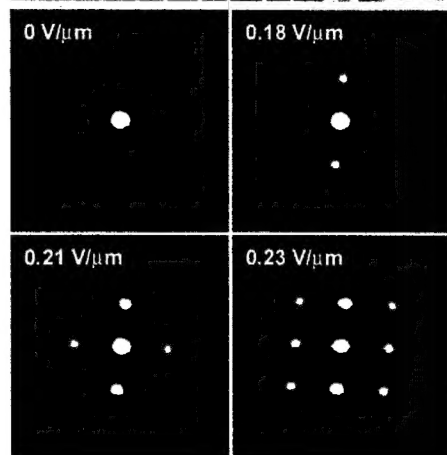
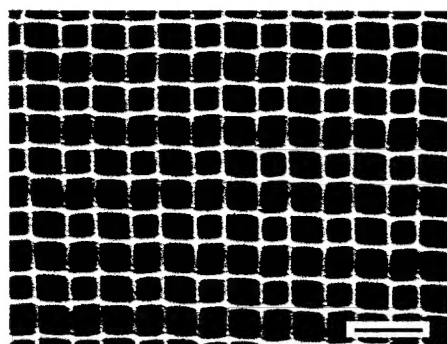


Figure 5: Polarizing microscope texture (top) and electrical response of a two-dimensional surface stabilized PSCDG.

the optical contrast of the grating basically disappears

and the grating is "OFF". Figure 4 shows an optical micrograph of a one-dimensional grating texture (the period is 5 microns) and the diffraction of a 633 nm laser beam in the ON (zero field) and OFF (3 V/ μ m) states for first order diffraction (0 represents the incident direction of the beam, +1 corresponds to a diffraction angle of 7.5°). The bottom part of the figure also shows the improvement in the ON state that can be achieved by biasing the field. Figure 5 shows the optical texture and performance of a two-dimensional grating stabilized by a surface network. In this case, significant response is seen at very low applied fields. In fact, significantly lower voltage operation (several tenths of a V/ μ m versus several V/ μ m) was a general result for gratings stabilized by surface networks. This is easily understood, since in the case of a bulk network the anchoring effect on the liquid crystal (scaling with surface area) is very much larger and distributed through the bulk. Hence a higher electric torque per

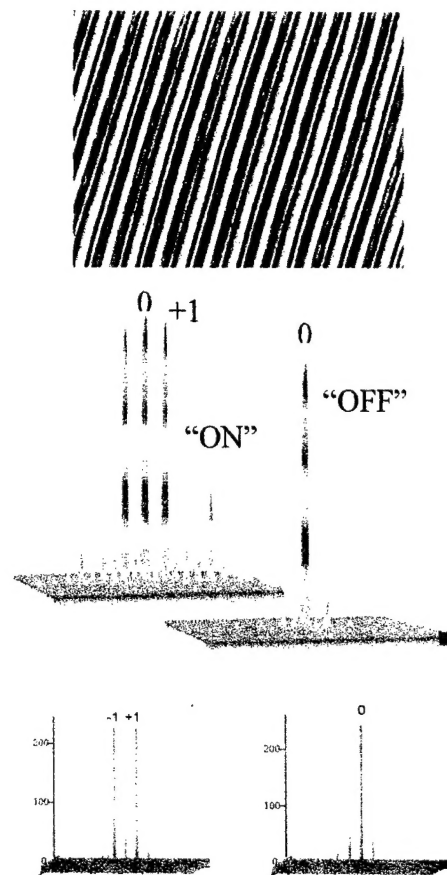


Figure 4: Electrically-switchable PSCDG.

unit volume is needed to switch the liquid crystal. Finally, we would like to point out that using a focused UV laser, we were also able to write arrays of switchable microgratings against a background of normal state cholesteric (see Figure 6).

Some nematic liquid crystals exhibit a dielectric anisotropy that undergoes a sign inversion as the frequency of an applied AC electric field of fixed amplitude passes through a threshold value (typically 15 kHz). We were able to make a frequency responsive polymer-stabilized grating out of one such material (MLC-2048, commercially available from Merck). Figure 7 demonstrates a preliminary result. Because the initial pattern forming state was not optimized and because of a poor match in index of refraction between the polymer and liquid crystal, a large number of diffraction orders was observed in the "ON" state (16 KHz at 3 V/ μ m), and the "OFF" state (10 KHz at 3 V/ μ m) was not very satisfactory. However, the principle of frequency-based switching is clearly demonstrated.

The response time of polymer-stabilized cholesteric liquid crystal gratings was determined by recording the change in the undiffracted beam intensity with time after switching from the "OFF" state (maximum undiffracted intensity) to the "ON" state (maximum diffracted intensity). This corresponds to a relaxation of the liquid crystal from homeotropic to diffracting state in zero applied field. There were two clear components to this relaxation: a fast component due to "free" liquid crystal not in close proximity to the network and a slower component tied to relaxation of the network itself. The former was characterized by a 1/e relaxation rate in the 1 to 10 msec range, while the latter required several hundred msec to relax. The trick is to minimize the network relaxation component; as Figure 8 shows, this can be done by again using a surface network to stabilize the liquid crystal diffracting state.

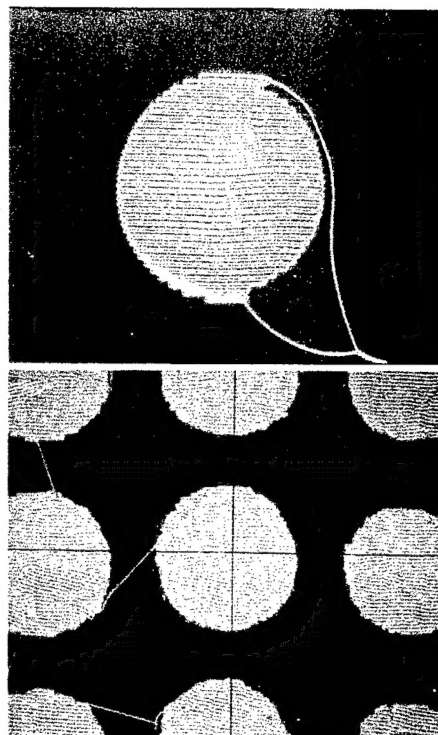


Figure 6: PSCDG microgratings. The grating diameter is 300 microns. The background is uniform cholesteric (helical axis vertical to the page).

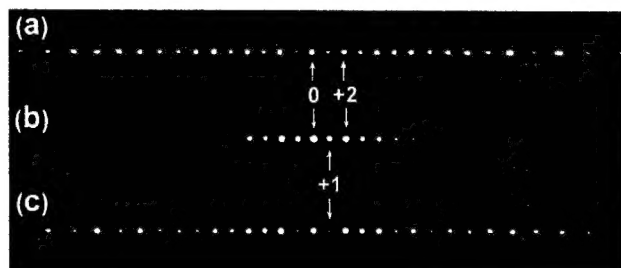


Figure 7: Frequency switchable PSCDG. State (b) obtained with a 10 KHz applied square wave, and (c) with a 16 KHz wave of the same amplitude.

The key advantages of our grating technology are low cost, simple and flexible processing, millisecond time / very low voltage response, and efficient phase and transmission (Raman-Nath) mode operation. All of these features are attractive for beam steering and optical switching applications. The main caveats are high polarization sensitivity (common

to all gratings deriving their contrast from optically birefringent materials) and as yet not thoroughly characterized aging against number of "ON-OFF" cycles and against extended operation at temperatures above 50°C. For the commercial liquid crystal mixtures used, the cholesteric phase is stable well above 100°C (and down to 0°C), but the robustness of the internal polymer network after repeated cycling over a large temperature range needs further investigation.

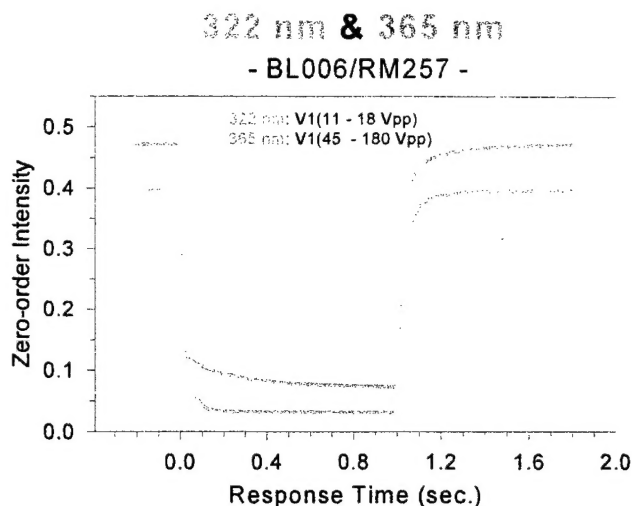


Figure 8: Dynamic response of PSCDG between OFF and ON states. Blue points correspond to a surface-stabilized PSCDG.

Liquid crystal-based polymer templating effect

Perhaps the most interesting scientific result of our work is the discovery of a remarkably efficient, self-organized templating effect, whereby a high degree of spatio-orientational order can be embedded in a polymer network by a pattern-forming liquid crystalline host. With the use of appropriate solvents, the liquid crystal can be almost completely removed, leaving behind a highly organized polymer structure that can be further processed. Combining this templating effect with the use of functional polymers – e.g., photonic or electronic polymers – opens some rather interesting possibilities. Because our patterning approach does not require an external means of generating the template (as in the case of photolithographic or holographic techniques), it is a significantly lower cost approach and does not depend on a particular polymerization process, such as a photoinitiated reaction, which severely limits the application of the photopatterning techniques. In fact, the polymerization of most semiconducting or photonic polymers requires some sort of chemical or thermal catalysis. A second crucial advantage of the liquid crystal templating approach is the patterning of high degree of polymer *orientational* order at the micro and mesoscopic length scales. The important properties of photonic and electronic polymers are known to be quite sensitive to orientational order, and it is no exaggeration to say that control of orientational order in the assembly of these polymers is just as decisive for ultimate applications as the design of the molecules themselves.

We have demonstrated the potential of the liquid crystal templating effect with the same mesogenic diacrylate (RM257) used in the diffraction gratings described previously. Figure 9 shows a gallery of templated polymer networks. The images are scanning electron micrographs taken after evacuation of the various liquid crystal templates (which corresponded to various pattern-forming states of a cholesteric) and opening of the sample cell. One and two-dimensionally patterned networks can be formed both as bulk structures and as surface layers. In the bulk case, one first notices the striking degree of

spatial patterning. We have determined that this derives from periodic gradients in the monomer concentration (*prior* to polymerization) patterned on spatially periodic gradients in the local orientation of the liquid crystal molecules that are characteristic of the different pattern forming states. Essentially the total free energy of the prepolymer

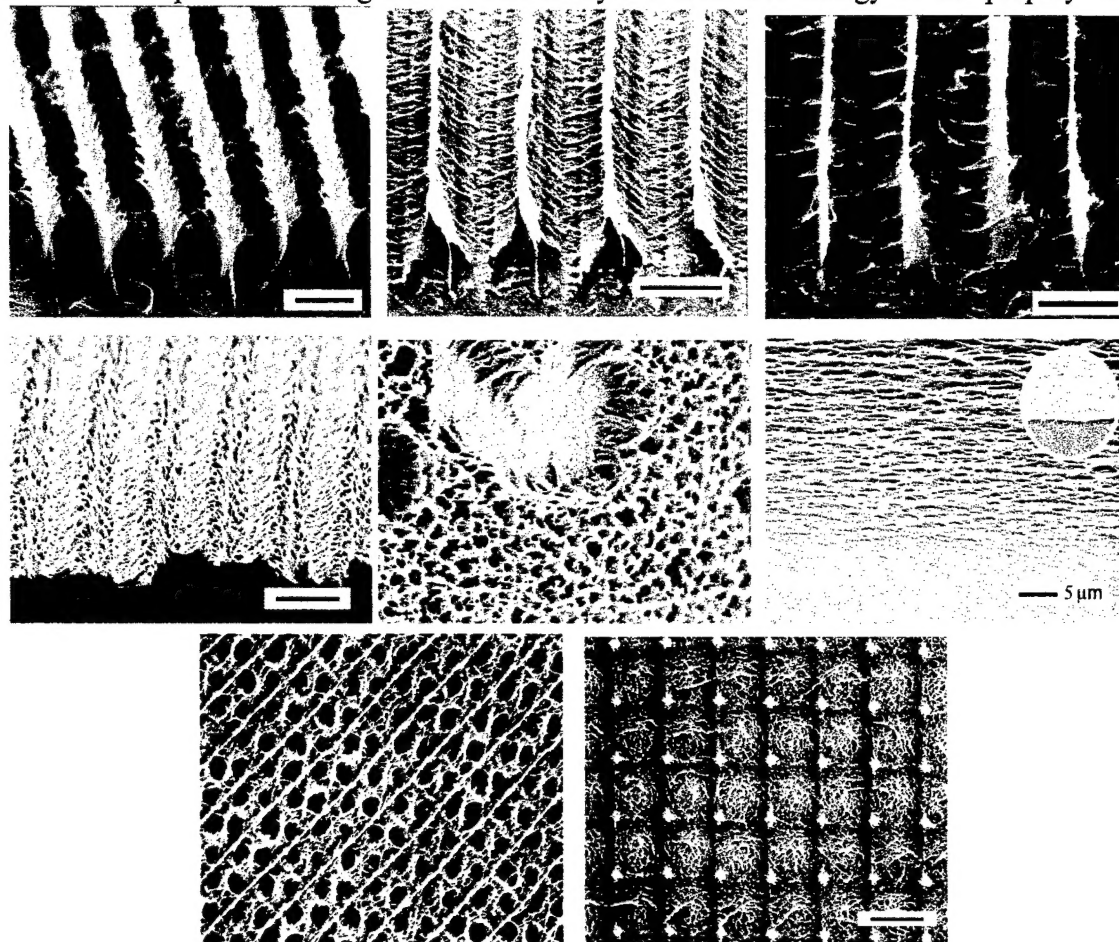


Figure 9: SEM images of various one and two-dimensional, bulk and surface, spatio-orientationally ordered polymer networks templated on pattern forming states of cholesteric and nematic liquid crystals. Scale bars represent 10 microns (except where otherwise indicated).

mixture is lowered when the monomer selectively replaces liquid crystal in regions of high (or low) orientational gradients of the latter.

The high degree of orientational order templated into the fibril structure making up the network is also quite striking, as the images in Figure 9 reveal. The formation of surface localized layers with high orientational order (both vertical and parallel to the surface) is compelling for applications involving functional polymers – for example, organic photovoltaics and supercapacitors, where orientational order and fibril morphologies with high surface to volume ratios are critical to enhancing the efficiency of electron or hole donor/acceptor layers and optimizing conductivity and the tradeoff between stored electrostatic energy and discharge time. The challenges that lie ahead are scaling the surface templating effect down from the micron to 100 nm scale – the thickness desirable for the aforementioned applications – and finding the correct combination of materials

and processing steps to enable the effective use of liquid crystal templating with functional polymers, ultimately achieving the high fidelity demonstrated with the mesogenic diacrylate RM257.

Liquid crystal-based patterning of conducting polymers

We have taken a first promising step toward addressing these challenges. In particular we have assembled networks of the acetylene derivative 1,6-heptadiyne in nematic and cholesteric hosts of the commercial liquid crystal BL006 (Merck) using a transition metal catalyst to carry out the polymerization. As Figure 10 indicates, we observe both spatial and orientational templating of poly(1,6)-heptadiyne (a dopable semiconducting polymer). We believe significant improvement of these early results is possible by carefully controlling temperature during the processing – specifically, formation of the liquid crystal template and introducing (and allowing diffusion of) the catalyst at a subambient temperature to prevent a premature or non-uniform reaction, and then raising temperature in a controlled fashion to initiate polymerization. A clever use of temperature gradients or local laser heating could also be used to produce surface localized networks or to assist in patterning.

Conclusion

Our research has taken us from demonstrating the effective use of polymers to stabilize novel, electrically responsive liquid crystal diffraction gratings to essentially turning the concept around: using the liquid crystal to build, in a remarkably simple way based on thermodynamic self-assembly, significant orientational and/or spatial order into a polymer network. In our view, the most interesting (though challenging) future

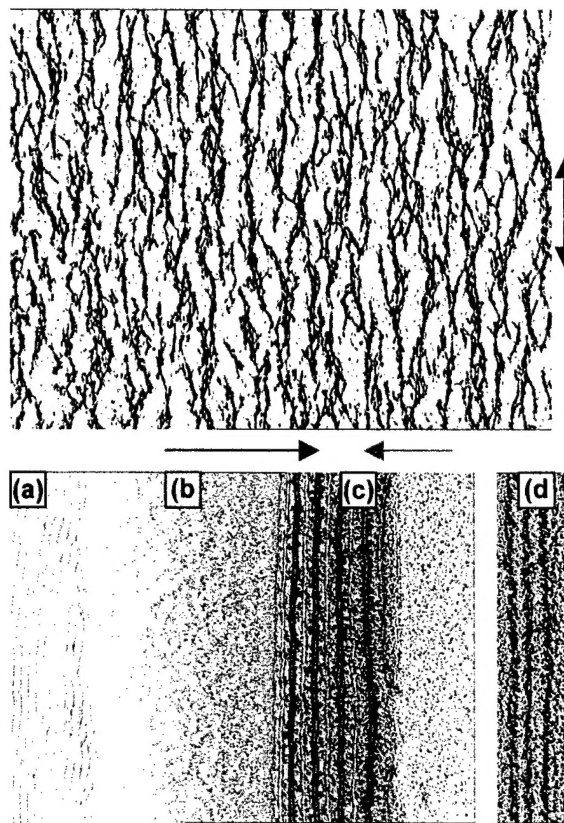


Figure 10: Top: Dopable poly(1,6-heptadiyne) network templated by a homogeneously aligned bulk nematic liquid crystal (alignment axis indicated by the double arrow), after removal of the LC solvent. The fibers are $\sim 2 \mu\text{m}$ diameter. The morphology is quite similar to what is observed when networks are formed in the same LC host from the diacrylates used to produce the surface localized structures in Figures 1 and 2. The diameter, aspect ratio, and space between fibers can likely be reduced by surface localized control of the polymerization reaction using the techniques described in the approach section. Bottom: Templating of dopable poly(1,6-heptadiyne) by a cholesteric LC host. (a) Unstabilized "fingerprint" texture. (b) Planar cholesteric texture stabilized by the polymer. (c) Stabilized "fingerprint" state. (d) After removal of LC, spatial patterning of the semiconducting polymer by is observed in the region shown in (c). Black arrow: Flow of LC/ catalyst mixture (prior to polymerization). Red arrow: Flow of LC/monomer mixture.

direction is to pursue the liquid crystal-based templating of functional polymer networks and of exotic functional colloids, such as quantum rods and fullerene tubes.

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